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Ionic Liquids as Thermal Energy Storage Media for Solar Thermal Electric Power Systems

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Contents

Solar Energy and Application

- Solar energy: Received on earth is about 5000 times greater than the sum of all other energy sources.
- Main application: Generate electricity.
- Problems: Solar energy availability depends on time, weather condition, and latitude, but electricity demand varies with time.
- Solution: Store the energy; originally from the solar radiation as thermal energy in storage fluid.

Thermal Energy Storage Media

- Molten salts: A mixture of $NaNO_3$, $NaNO_2$, and KNO_3.
  - Main problem: Melting point is about 142^{o}C, resulting in freezing in the pipeline in the evening and causing high operation costs.
- Thermal oil: The organic oil such as Santotherm 55.
  - Main problem: Limited temperature range, usually below 300^{o}C; Low density and low heat capacity require higher storage volume and higher construction costs.

Properties of Ionic Liquids

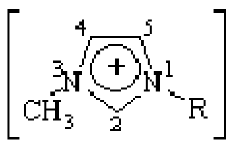
- Low melting-point solvents.
- High ionic concentration.
- Wide temperature range for liquid.
- Non-volatile and non-toxic solvents.
- Wide electrochemical windows, up to 4.0 Volts.

Types of Ionic Liquids

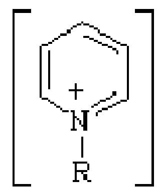
- Formation of Ionic liquids:

e.g.: $$C_4mimCl + HPF_6 \Rightarrow C_4mimPF_6 + HCl$$

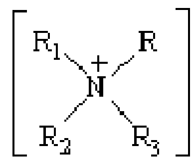
Most Commonly used cations



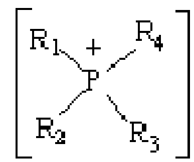
1-alkyl-3-methyl-imidazolium



N-alkyl-pyridinum



Tetraalkyl-ammonium



Tetraalkyl-phosphonium

($R_{1,2,3,4}$ = alkyl)

Some Possible anions: Water - insoluble → Water - soluble

Water - insoluble		Water - soluble
$[PF_6]^-$	$[BF_4]^-$	$[CH_3CO_2]^-$
$[(CF_3SO_2)_2N]^-$	$[CF_3SO_3]^-$	$[CF_3CO_2]^-$, $[NO_3]^-$
$[BR_1R_2R_3R_4]^-$		Br^-, Cl^-, I^-
		$[Al_2Cl_7]^-$, $[AlCl_4]^-$ (decomp.)

Most commonly used alkyl chains: ethyl, butyl, hexyl, octyl, decyl

Experimental

- Synthesis of ionic liquids
  - $C_{10}mimPF_6$, C_8mimPF_6, C_4mimPF_6, $C_{10}mimBF_4$, C_8mimBF_4, C_4mimBF_4, C_4mimTf_2N, and $C_4mim\text{-}AlCl_4$
- Characterization of the synthesized ionic liquids
  - TGA, DSC, and NMR
- Measurement of the properties of ionic liquids
  - melting points, decomposition temperature, viscosity, and density

Some Properties of Ionic Liquids

Ionic liquid	Melting point,°C	Decomposition point, °C	Viscosity at 25°C, mPa s	Density at 25°C, kg/m^3
$[C_{10}mim][PF_6]$	34	390	--	--
$[C_8mim][PF_6]$	-75	416	--	1400
$[C_4mim][PF_6]$	4	390	312	1370
$[C_{10}mim][BF_4]$	-77.5	--	--	--
$[C_4mim][BF_4]$	-75	407	219	1119
$[C_4mim][CF_3(SO_2)_2N^-]$	-89	402	54.2	1429

Properties of Heat Transfer Fluids

Commercial name		Chemical composition	Liquid T, (°C)	Thermal conductivity (W/m K)	C_p (kJ/kg K)	Viscosity (10^{-6} m^2/s)	Volume expansion (10^{-4} K^{-1})	Specific gravity
Propylene glycol	Dowfrost (Dow) 59 wt% aq.soln.	Propylene glycol K_2HPO_4 1%	-31~102	0.39	3.6 at 27°C	3.0 at 38°C 70 at -18°C	7.3	1.033 at 27°C
Ethylene glycol	Dowtherm SR-1 (Dow) 59 wt% aq.soln.	Ethylene glycol K_2HPO_4 2%	-37~110	0.42	3.4 at 27°C	2.6 at 100°C 61 at 38°C	6.3	1.074 at 20°C
Polyglycols	UCON 500 (Union Carbide)	Polyglycol 90% inhibitor	-37~289	0.15	2.2 at 100°C	11.5 at 100°C 61 at 38°C	7.9	0.98 at 100°C
Paraffinic hydrocarbon oils	Caloria HT 43 (Exxon)	Petroleum distillate	-9.5~311	0.13	2.1 at 100°C	5.0 at 100°C 31 at 38°C	10.0	0.80 at 100°C
Synthetic Hydrocarbon oils	Brayco 888 HF (Bray Oil Co.)	Polymerized 1-decene	-85~227	0.13	2.3 at 25°C	4.5 at 100°C 22.5 at 38°C	4.8	0.83 at 15°C
Silicone oils	Syltherm 444 (Dow Corning)	Polydimethy-siloxane	-46~>315	0.14	1.6 at 100°C	7.0 at 100°C 20 at 25°C	10.7	0.95 At 25°C
water		H_2O	0~100	0.6	1.6 at 100°C	0.3 at 93°C	2.1	1.00 At 4°C
Ionic Liquid		$[C_8mim][PF_6]$	-75~416	--	2.5 at 25°C	---	--	1.4 at 25°C

Properties of Molten Salt, Thermal Oil and Ionic Liquid

Properties at 25°C	molten salt 60%$NaNO_3$, 40%KNO_3	Thermal oil Santotherm 55	Ionic liquid C_8mimPF_6
Density, kg/m^3	--	886.2	1400
Specific thermal capacity C_p, J/kg K	--	1907	2500
Temperature range for liquid, °C	220 to 600	-30 to 300	-75 to 416
Storage density, MJ/m^3	--	59	378
Thermal conductivity k, W/m K	--	0.1891	--
Dynamic viscosity, μ, Pa s	--	0.0105	--
Prandlt number, Pr = Cp μ/k	--	160.5	--

TES Capacity of Ionic Liquids

- For C_8mimPF_6, the liquid temperature range is –75 to 416°C, heat capacity C_p=2500 J/kg K, and density ρ=1400 kg/m^3. When T_{inlet} = 210°C and T_{outlet} = 390°C, the TES density (E) can be calculated as follows:

$$E = \rho C_p (T_{out} - T_{in})$$

$$= 1400 \frac{kg}{m^3} \times 2500 \frac{J}{kg\ K} \times (663 - 483)K$$

$$= 378 \times 10^6 \frac{J}{m^3} = 378 \frac{MJ}{m^3}$$

Optimization of Ionic Liquids

- Various anions and cations of ionic liquids were combined for optimized melting points and thermal stability.
- Different ionic liquids were mixed for optimized compositions which show a higher decomposition temperature than each individual ionic liquid.
  - E.g.: 50% [C_4mimBF_4] (T_{dec} = 407°C)
    + 50% [C_6mimTf_2N] (T_{dec} = 341°C)
    $\Longrightarrow$ Ionic liquid mixture (T_{dec}= 427°C)

Effect of anions on IL melting point

Ionic liquid	Melting point, ^{o}C
[emim][NO_3]	38
[emim][NO_2]	55
[emim][$MeCOO^-$]	-45
$[emim]_2[SO_4]$	70
[emim][PF_6]	58-60
[emim][$CF_3SO_3^-$]	-9
[emim][$CF_3(CF_2)_3SO_3^-$]	28
[emim][$(CF_3SO_2)_2N^-$]	-3
[emim][CF_3COO^-]	-14
[emim][$F(HF)_n^-$]	-90

Cost Comparison of Thermal Energy Storage Media

Liquid Media	Media cost per kg, \$/kg	Media cost per kWh_t, \$/kWh_t
Mineral oil	0.30	4.2
Synthetic oil	3.0	43
Silicone oil	5.0	80
Nitrite salts	1.0	12
Nitrate salts	0.7	5.2
Carbonate salts	2.40	11
Liquid sodium	2.00	21
Ionic liquid	1.5 to 7	--

Evaluation of IL

- Novelty:
  - Use of IL as TES media is new.
- Potential market:
  - Industrial solar thermal systems:
    - For a solar power plant of 10,000 kW, the tank volume is about 1,500 m^3.
    - Assuming IL cost of \$1.5~7/L, the total cost of TES media will be 2.25 to 10.5 million.

Conclusions

- Ionic Liquids have excellent thermal properties for use as TES media and heat transfer media for solar thermal power plant system.
- For C_8mimPF_6 ionic liquid, the TES density is 378 MJ/m^3 and liquid temperature range is –75 to 416^oC.
- Low viscosity and high thermal conductivity make ionic liquids as excellent TES media candidates.
- Economic feasibility of ionic liquids as liquid TES media and heat transfer media needs further investigation.

Acknowledgements

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